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ORGANIC-MINERAL MATTER INTERACTIONS IN GREEN RIVER OIL SHALE

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INTRODUCTION

The nature of the association between kerogen or bitumen and the mineral matter phase in oil shales has not been well characterized, yet these interactions are fundamental to any proposed separation and oil recovery procedure. Analogous information has been reported concerning marine sediments (1), but relatively little data are currently available relevant to the organic-mineral matter interaction in oil shales (2-5). Therefore, this study proposed to investigate this problem using a chemical extraction procedure with spectroscopic (FTIR and NMR) identification of the various separated fractions.

Samples of Colorado Green River oil shale (C-a tract, Mahogany zone) were treated in a series of acid/ether extractions in order to preferentially disassociate the mineral matter phase. It is known that carbonate minerals are dissolved by HCl solutions and that pure HF or HF/HCl mixtures effectively remove silicate minerals, quartz, and clay minerals (6, 7). Bitumen, the organic fraction soluble in the common organic solvents, was removed by the Soxhlet extraction method. The fraction of the total mineral content encapsulated by kerogen and thus not accessible to an acid treatment is estimated to be insignificant based on the results obtained by this study.

The relative amounts of acid/ether extracted organics isolated with both the carbonate and silicate minerals were determined. In addition, it was noted that certain fractions of the bitumen were trapped by these two mineral constituents. On the basis of these data, inferences are made concerning possible types of bonding between kerogen and the inorganic mineral matter matrix.

EXPERIMENTAL

The chemical extraction procedure is summarized in flowchart form in Figure 1. A series of acid and ether extractions were used to treat samples of Colorado Green River oil shale (C-a tract Mahogany zone) of three different richnesses: 25, 31, and 44 GPT. These samples were prepared, first, by standard pulverizing and sieving procedures of mine-run oil shale and then, by separation according to organic content using the heavy media liquids gravitational separation technique (8). The final mesh size was 100 x 200.

Bitumen was extracted from dried oil shale using the Soxhlet procedure: 7:3 mixture of benzene:methanol. The resulting fraction was treated with 6N HCl and any iron contamination introduced during the initial grinding step was removed by mechanical magnetic separation. The HCl aqueous phase was further extracted with NaOH yielding three fractions of different acidities: pH = 1, 6.5, >11.

The bitumen, carbonate-free oil shale was neutralized to pH ~5 and the Soxhlet extraction procedure repeated to completely remove physically trapped bitumen. The remaining shale was extracted with a 3:1 mixture of 50% HF:6N HCl followed by an ether extraction and separation of three pH fractions. The Soxhlet extraction procedure was again repeated.

The effectiveness of the chemical extraction procedure was monitored by elemental analysis results obtained by DC arc emission spectroscopy (ARL Model 2100 Film 2m Emission Spectrograph). The structural composition of the various filtrate fractions was characterized using both FTIR (Digilab FTS-20E) and NMR (FT80A, Varian Associates) spectroscopy. In addition, the mineral and elemental compositions of the original oil shale samples were determined from X-ray diffraction (Phillips APD-3500) and energy dispersive X-ray fluorescence (Kevex Model 0700) data. Low-temperature ash samples were prepared using a 13.56 MHz radio frequency asher (LFE Corporation, Model LTA 504).

RESULTS AND DISCUSSION

Bulk Mineralogical Composition

Elemental analysis of organic C, H, N, O, and S concentrations indicated that 13-23% of the

original Green River oil shale samples was organic matter. The remaining 77-87% consisted of various minerals, primarily ankerite, dolomite, aragonite, quartz, albite, analcime, and illite (see Table I). A concentration dependence as a function of shale richness was found for certain types of minerals. For example, the relative concentrations of clay minerals (illite/smectite) and to a certain extent albite increase with increasing organic carbon content, whereas minerals such as calcite and aragonite are characterized by an inverse relationship.

The low-temperature ash results for the clay mineral constituents were opposite to the expected trend exhibited by the remaining minerals. The clay mineral concentration was found to decrease with low-temperature ashing in contrast to the concentrations of the other minerals which increased in proportion to the organic content removed by the ashing procedure. This irregular feature may be attributed to layer collapse as a result of either organic oxidation (9) or the removal of an associated water phase.

TABLE I
BULK MINERALOGY OF GREEN RIVER FORMATION Ca-TRACT,
MAHOGANY ZONE, OIL SHALE IN WEIGHT PERCENT

Sample Richness (GPT)	Analcime	Clay ^a	Quartz	Feldspar		Ankerite/ Dolomite	Calcite	Pyrite	TDI ^b	Trace
				Kspar	Albite					
25 Orig	14	8	14	6	5	30	14	<1	.34	Siderite
25 LTA	18	7	13	8	9	29	14	<1	.44	Gypsum
31 Orig	12	10	16	<1	10	29	7	<1	.42	Gypsum
31 LTA	19	7	14	<1	18	31	10	<1	.34	Aragonite
44 Orig	10	19	15	<1	13	20	2	2	.53	Marcasite
44 LTA	14	8	17	<1	24	28	4	2	.75	

a. Clay minerals consist primarily of a mixed layer illite/smectite.

b. Total diffracting intensity, the sum of all fractions before normalization.

Chemical Extraction Results

The HCl extraction step effectively separated carbonate minerals from the oil shale samples as indicated by elemental analysis data summarized in Table II. Approximately 99% of the elemental Ca and approximately 94% of the Mg in the 44 GPT oil shale were removed. On the basis of experimental results of the HCl/ether extracts, it was determined that at least 0.45 and 0.38 wt% of the total organics in the 25 and 44 GPT dried oil shale, respectively, are recoverable (see Table III). Therefore, there appears to be a rather intimate association between this organic fraction and the carbonate mineral matrix. It is also reported that 3.40 and 3.65 wt% of the total organics in these same two samples are trapped by the carbonate mineral matrix and only released after the HCl acid treatment.

The second acid extraction step, leaching by HF/HCl, was equally effective, resulting in the separation of approximately 96% of the elemental Si and approximately 86% of the Al (see Table II). The total amount of organics extracted by the HF/ether combination was at least 1.72 and 1.34 wt% of the initial total organic content of the 25 and 44 GPT samples, respectively. Physiosorption by the silicate mineral matrix occurred to the extent that 1.64 and 2.00 wt% of the total organics were trapped yet recoverable by the third Soxhlet extraction. The results of the preferential disassociation procedure are summarized in Table III.

It is determined that approximately four times more bitumen-free organic matter is associated with the silicate mineral matrix than with carbonate minerals. This organic matter is judged to be an interfacial layer between kerogen and the inorganic mineral matrix. The inter-layer structures isolated with either the carbonate or silicate minerals have slightly modified properties compared to the bulk kerogen material due to the presence of mineral binding forces and therefore, are more properly classified as a form of kerogen. The greater majority of the bitumen portion of these Green River oil shale samples was removed by Soxhlet extraction.

It was determined that 27-32 wt% of the bitumen is physically trapped by the mineral matter matrix and to a larger extent by carbonate than silicate minerals. These results are in support of a previous study (3) which suggested a strong interaction between carbonate minerals and carboxylic acid functional groups in Green River oil shale bitumen. In addition, both high-pressure CO₂ dis-aggregation (4) and cation exchange (5) experiments have indicated a close coupling between the mineral matrix and bitumen. The bitumen fractions separated in this work during the chemical

treatment were not specifically analyzed for various chemical components, but the Fischer Assay results summarized in Table III indicate a relatively strong association, particularly in the form of physical trapping, between bitumen and the carbonate mineral matrix.

TABLE II
MULTI-ELEMENTAL ANALYSIS (WT%) OF ORIGINAL AND TREATED
GREEN RIVER OIL SHALE SAMPLES^{a, b} (44 GPT SAMPLE)

Element	Original Oil Shale	Benzene/Methanol Treated Oil Shale	HCl-Treated Oil Shale	HF/HCl-Treated Oil Shale
Weight Fraction	100.0	97.1	68.6	29.6
Al	6.4	5.9	4.6	0.64
As*	87.1 ppm	88.1 ppm		
B	0.021	0.015	0.013	
Ba	0.11		0.08	0.05
Ca	5.1	5.2	0.04	0.04
Cr	0.03	0.03	0.01	0.01
Cu	0.003	0.004	0.003	0.003
Fe	3.6	3.7	1.2	0.96
K	1.9	2.0	1.2	0.23
Mg	4.4	4.5	0.18	0.17
Mn	0.083	0.074	0.013	0.006
Mo				0.005
Na	0.57	0.59	0.04	0.04
Ni	0.018	0.015	0.009	0.003
Si	15	15	14	
Sr	0.08	0.07		0.01
Ti	0.28	0.30		0.07

a. DC Arc Emission Spectroscopy, values given in wt%

b. Mahogany zone C-a tract, 100 x 200 mesh oil shale

* Instrumental Neutron Activation Analysis

TABLE III
ORGANIC MATTER DISTRIBUTION OF TREATED OIL SHALE
EXTRACTS^a BASED ON WT% OF TOTAL ORGANICS

	25 GPT Oil Shale	31 GPT Oil Shale	44 GPT Oil Shale
Bitumen I	13.48	16.14	11.80
II	3.40	3.44	3.65
III	1.64	0.05	2.00
Total Bitumen	18.52	19.63	17.45
Carbonated Associated Organics			
Ether Extract I A/N	0.15	0.18	0.18
Ether Extract I N	0.21	0.19	0.13
Ether Extract I B	0.09	0.11	0.07
Total Extracts I	0.45	0.48	0.38
Silicate Associated Organics			
Ether Extract II A/N	1.33	0.26	0.50
Ether Extract II N	0.09	0.17	0.62
Ether Extract II B	0.30	0.02	0.22
Total Extracts II	1.72	0.45	1.34

a. Total organic concentrations based on elemental analysis are determined to be 13.46, 16.24, 22.93 wt% for 25, 31, and 44 GPT oil shales, respectively.

Spectroscopic Analysis

During the chemical extraction procedure, several major IR bands were monitored in order to determine the extent, if any, of chemical rearrangement. Various references in the literature

have cited the reaction of both hydrochloric and hydrofluoric acids with organic compounds resulting in the modification of specific chemical properties. These reactions include, for example, the hydrolysis and addition reactions of quinones, esters, and olefins with HCl (10,11) in addition to condensation reactions involving HF and olefinic and aromatic compounds (11). The spectroscopic data of the filtrate fractions indicated that HCl or HF generated reactions did not occur to an appreciable extent and that insignificant chemical rearrangement occurred. This is an important point, since it implies that the recoverable organic matter associated with either the carbonate or silicate mineral matrix is of the form which constitutes the *in situ* interfacial layer between kerogen and the inorganic mineral matrix.

FTIR characterization of oil shale was based on the assignment of several IR bands (12) and their respective absorbances (13) (see Table IV). These results, in addition to NMR data discussed below, indicate several similarities as well as differences in the structural composition of the organic matter associated with either mineral constituent studied here. A comparison of FTIR spectra of two ether extract fractions is shown in Figure 2. Both sets of ether extracted organic matter contained trace amounts of molecular water, alcohols, and aromatic compounds. The tentative assignment of the 1125 and 1030 cm^{-1} bands to aryl-alkyl ether groups (14) suggests a preferential silicate--aryl-alkyl ether association, since these bands were identified in the HF/HCl fractions but not in the HCl fractions.

The major constituent of the acid/ether extracted organics was determined to be paraffinic compounds. The $[\text{CH}_3]/[\text{CH}_2]$ ratios determined from FTIR spectra were found to increase with increasing pH for the ether extracted organics associated with the silicate mineral matrix: 0.40, 0.44, and 0.54. This result suggests that the more highly branched compounds and/or the small molecules isolated with the silicate minerals are weaker Lewis acids. The relatively high $[\text{CH}_3]/[\text{CH}_2]$ ratios reported are consistent with the high hydrogen content of Green River oil shales (atomic H/C ~ 1.5 -1.6). This property is also attributed to the observation of a strong band at 720 cm^{-1} due to skeletal vibrations of long chain aliphatic molecules. A relatively higher concentration of aliphatic chains was found in the organic group associated with the silicate mineral matrix.

TABLE IV
IR BAND ASSIGNMENTS

ν (cm^{-1})	Vibrational Mode
3430	OH stretch
3100-3000	CH stretch (aromatics)
2962	Asymmetric CH_3 stretch
2930	Asymmetric CH_2 stretch
2872	Symmetric CH_3 stretch
2860	Symmetric CH_2 stretch
1735	C=O stretch (esters)
1712	C=O stretch (ketones, aldehydes)
1630	C=O stretch (bridged quinones)
1620	C=C stretch
1455	Asymmetric CH_2 and CH_3 bend
1185	C-O stretch
1125, 1030	C-O vibration (aryl-alkyl ethers)
890	$\text{CH}_2=\text{C}$ bend
870, 820, 750	Out of plane deformation aromatic CH
720	Skeletal vibration, straight chains >9 CH_2

A correlation between the C=C stretching vibration and the carbonate mineral matrix was established. Although approximately a tenth as intense as the CH_3 symmetric bending vibration, the 1620 cm^{-1} band due to C=C stretching was identified in all three HCl extracts but in none of the HF/HCl spectra. Further evidence of a preferential association between olefinic hydrocarbons and carbonate minerals was provided by the significantly larger $\text{CH}_2=\text{C}/\text{CH}_2 + \text{CH}_3$ ratio in the case of the HCl spectra. These data are in contrast to the results obtained by Spiro (2) for some Israeli oil shales which reported relatively higher C=C/ CH_3 absorbance ratios for organic matter associated with silicates, suggesting a preferential silicate-olefin interaction. This discrepancy may be attributed to the choice of different oil shales used in both studies.

On the basis of the C=O and C-O stretching vibrations of ester functional groups, a major distinction was determined concerning ester-mineral matter interactions. Significantly larger concentrations of esters were identified in the HF/ether extracts indicating a closer association between esters and silicate minerals. In addition to esters, a relatively larger ketone and aldehyde

content was found with those organics associated with the silicate mineral matrix. The results of Spiro (2) are inconclusive concerning a preferential ester-mineral matter association.

The aromatic content of the original oil shale was determined by NMR spectral analysis to be considerably larger than that of the acid extracted organics. This result is consistent with FTIR data. The NMR results summarized in Table V for the 44 GPT sample also indicate that the aromatic content of the bitumen fraction separated in the first Soxhlet extraction is lower than that of the original oil shale but comparable to that of both sets of acid/ether extracts. However, distinct spectral differences were observed between the initially separated bitumen and the neutral organic fraction isolated with the silicate minerals (see Figure 3). From these differences it can be concluded that the organic matter recovered from the ether extracts of the HCl and the HF/HCl mixture subsequent to the initial Soxhlet extraction is not residual bitumen. The majority of the bitumen was removed initially in the extraction procedure and the organic matter isolated in association with carbonate and silicate minerals is a portion of the kerogen-mineral matter interfacial layer.

TABLE V
¹H-NMR SPECTROSCOPIC ANALYSIS

	<u>Aromatic</u>	<u>Paraffinic</u>
Total Organics in Oil Shale	~20%	~80%
H ₂ O Soluble Organics	<0.1%, mainly monoaromatics	>99%, some olefins, some polar (possibly ester)
Bitumen I	~5.2%, mono and diaromatics	94.8%, methyl, alkyl substituted paraffinic chains (>C ₁₆), 2/3 paraffinic and 1/3 naphthenic
Carbonate Associated Organics ^a		
Ether Extract I, A/N	~3%, mainly monoaromatics	~97%, branched paraffins
Ether Extract I, N	~2%, mainly monoaromatics	~98%, branched paraffins some olefins
Ether Extract I, B	0.2%, mostly diaromatics	~99.8%, highest [CH ₃]/[CH ₂], some olefins
Silicate Associated Organics ^a		
Ether Extract II, A/N	~3%, mono and diaromatics	~97%, paraffinic chains (~C ₁₀), some conjugated olefins
Ether Extract II, N	~1.8%, mainly monoaromatics	~98.2%, small molecules, regularly repeating structural type ~1% olefins
Ether Extract II, B	~1.8%, mainly monoaromatics	~98.2%, long-chain paraffins (~C ₁₀), polar-functional groups

a. Abbreviations: A/N - acidic/neutral, N - neutral, B - basic

Both NMR and FTIR results indicated that the organics associated with carbonate minerals and those associated with silicate minerals are predominantly of paraffinic composition. The NMR data identified approximately equal relative aromatic concentrations in both sets of organic matter in disagreement with Spiro's (2) results for Israeli oil shales. In contrast, Spiro's (2) data indicated that organic matter associated with silicate minerals is composed of relatively more aromatic as well as more polar compounds in comparison to the organic-carbonate group. As mentioned above concerning the FTIR data, this apparent difference in aromatic content between Colorado and Israeli oil shales may be the result of dissimilar mineralogical compositions and/or geochemical properties of the two oil shales (15,16).

The paraffinic carbon composition was determined to be similar for both groups of acid/ether extracted organics. The relative concentrations of mono- and diaromatic compounds were also comparable. In addition, the NMR analysis identified chain lengths of about C₁₀ with those organics associated with silicate minerals and branched paraffins with the carbonate mineral group. Long chain lengths and branched compounds having a high CH-activity are two important factors which have been reported to affect adsorption processes (17,18). Therefore, it is not inconceivable that adsorption or a slightly stronger trapping interaction is responsible for certain types of organic-mineral matter bonding.

Organic-Mineral Matter Interactions

The results obtained by this study seem to suggest an equal preference for chemical bonding

as for physisorption. Although one or the other type of interaction cannot be definitively excluded, several inferences are possible. The presence of substantial concentrations of esters in the silicate-organic matter group suggests strongly bonded ester-silicate complexes. However, there remains the possibility that the ester functional group may be providing the linkage necessary for adsorption. Physisorption of esters by the silicate mineral matrix cannot be ruled out, but appears to be rather unlikely considering the bonding forces usually associated with this functional group.

The organic matter-carbonate mineral interaction may preferentially involve chemical bonding between energy rich olefinic functional groups and minerals such as CaCO_3 and $\text{CaCO}_3\text{MgCO}_3$. The relatively large concentration of branched paraffins identified with the carbonate mineral group would seem to suggest an adsorption type of interaction on the basis of these compounds' high CH-activity. Similarly, adsorption of long chain aliphatic compounds on silicate minerals is inferred from the NMR results. In the last two cases, physisorption is also possible, but adsorption and physisorption would seem to be more likely than the formation of chemical bonds. However, hydrogen bonding and other similar covalent or ionic interactions cannot be disregarded. The specific organic structures identified are a portion of the interfacial layer formed between kerogen and the mineral matter, and thus, the possible associations discussed in this section refer to interactions between the carbonate and silicate minerals and a form of kerogen.

SUMMARY

The problem of organic-mineral matter bonding, particularly that involving kerogen, although at first glance rather intractable, has been partially reduced in scale by the data presented here. The chemical extraction technique outlined earlier proved to disassociate successfully in a step-wise manner both carbonate and silicate minerals from several oil shale samples of different richness. The organic matter recovered subsequent to the initial Soxhlet extraction was shown to be bitumen-free.

It was determined that approximately four times more bitumen-free organic matter is associated with silicate minerals than with carbonate minerals. The major structural constituent of the various filtrate fractions was paraffinic compounds. However, spectroscopic analysis indicated relatively larger concentrations of olefins and branched paraffins with the acid/ether extracted organics associated with the carbonate minerals. The silicate mineral matrix was determined to interact with a bitumen-free organic interfacial layer containing relatively more esters, ketones, and long chain aliphatic compounds. In addition, trapping of bitumen-free organic matter was observed, particularly in the case of the carbonate mineral matrix. These interactions involving carbonate and silicate minerals are descriptive of the binding forces in Green River oil shale as they pertain to the interfacial layer between kerogen and the inorganic mineral matrix.

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Figure 1.
 Preferential organic-mineral matter
 disassociation by chemical methods

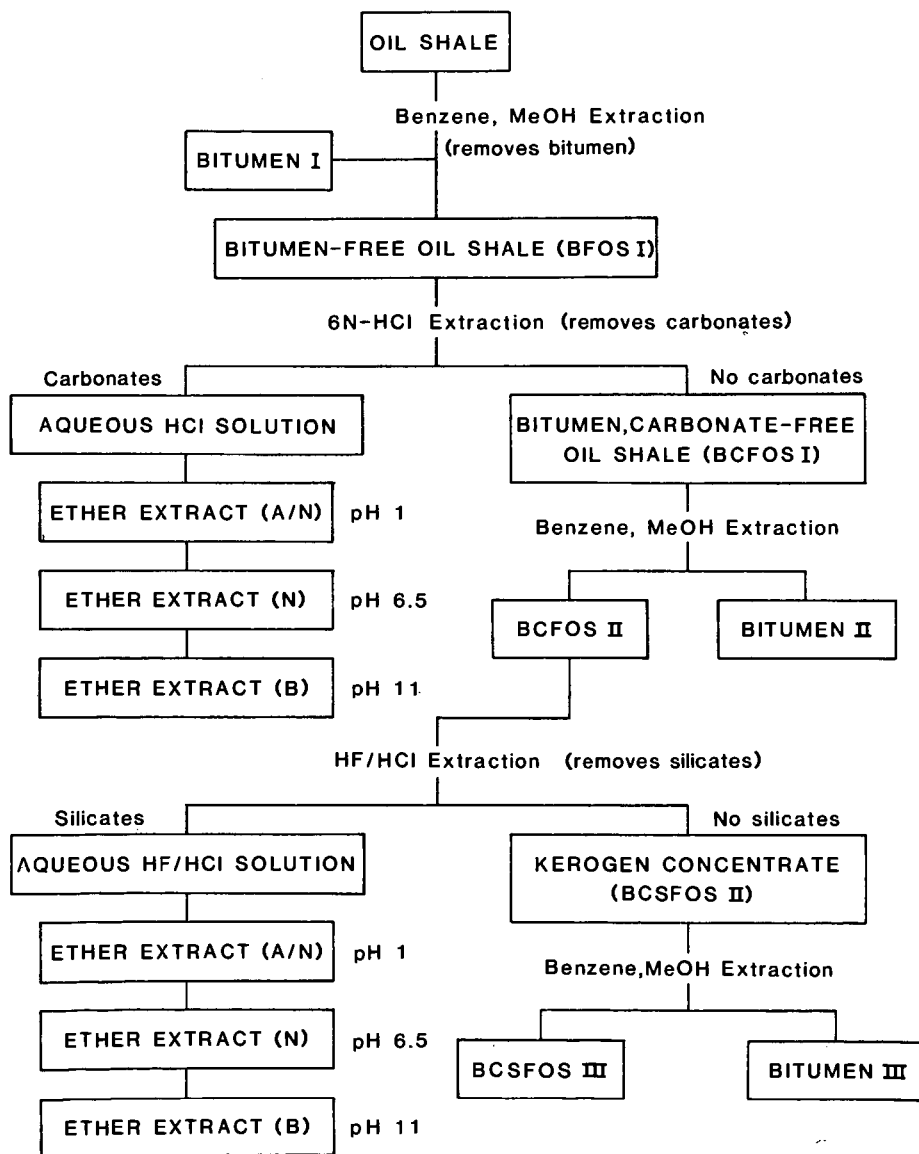


Figure 2. FTIR Spectra of ether extracted (at pH 6.5)
HCl (a) and HF (b) fractions (44 GPT Sample)

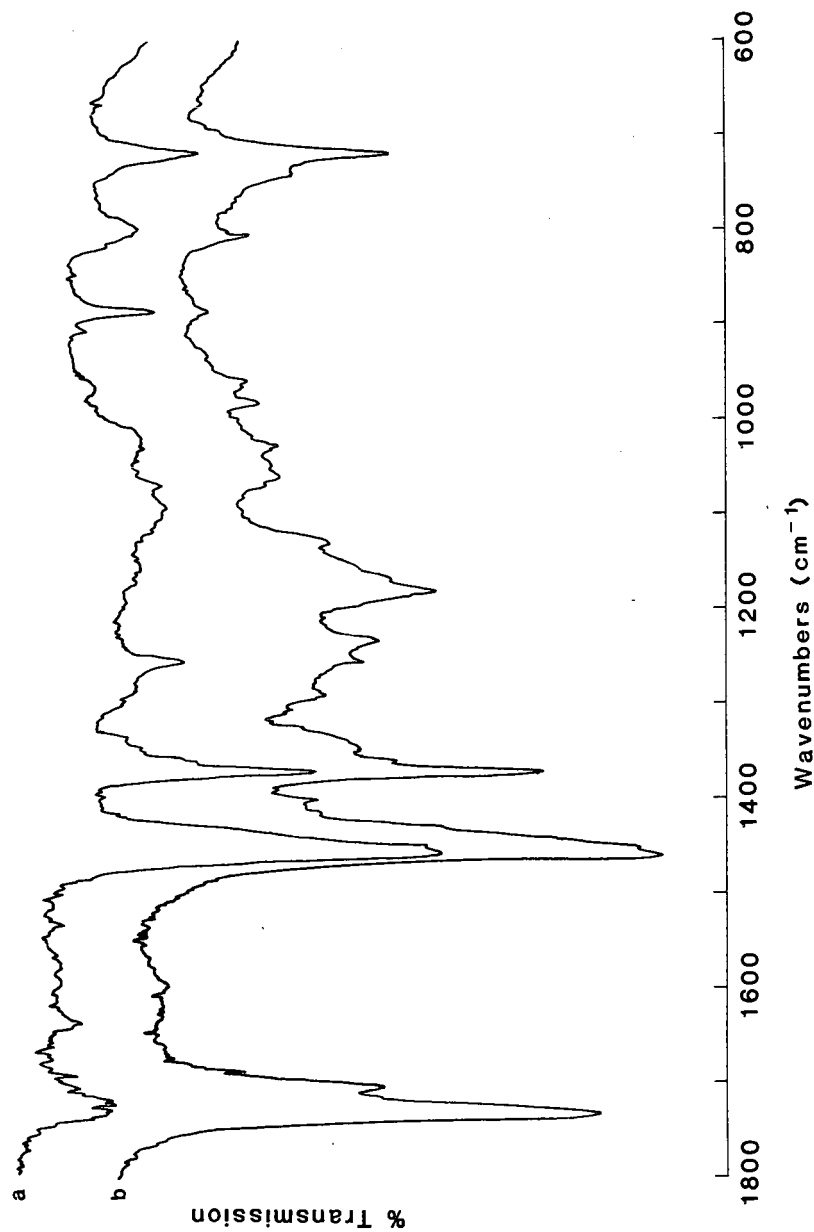


Figure 3a. ¹H-NMR Spectrum of neutral ether extracts
of HF/HCl treated oil shale filtrate (44 GPT Sample)

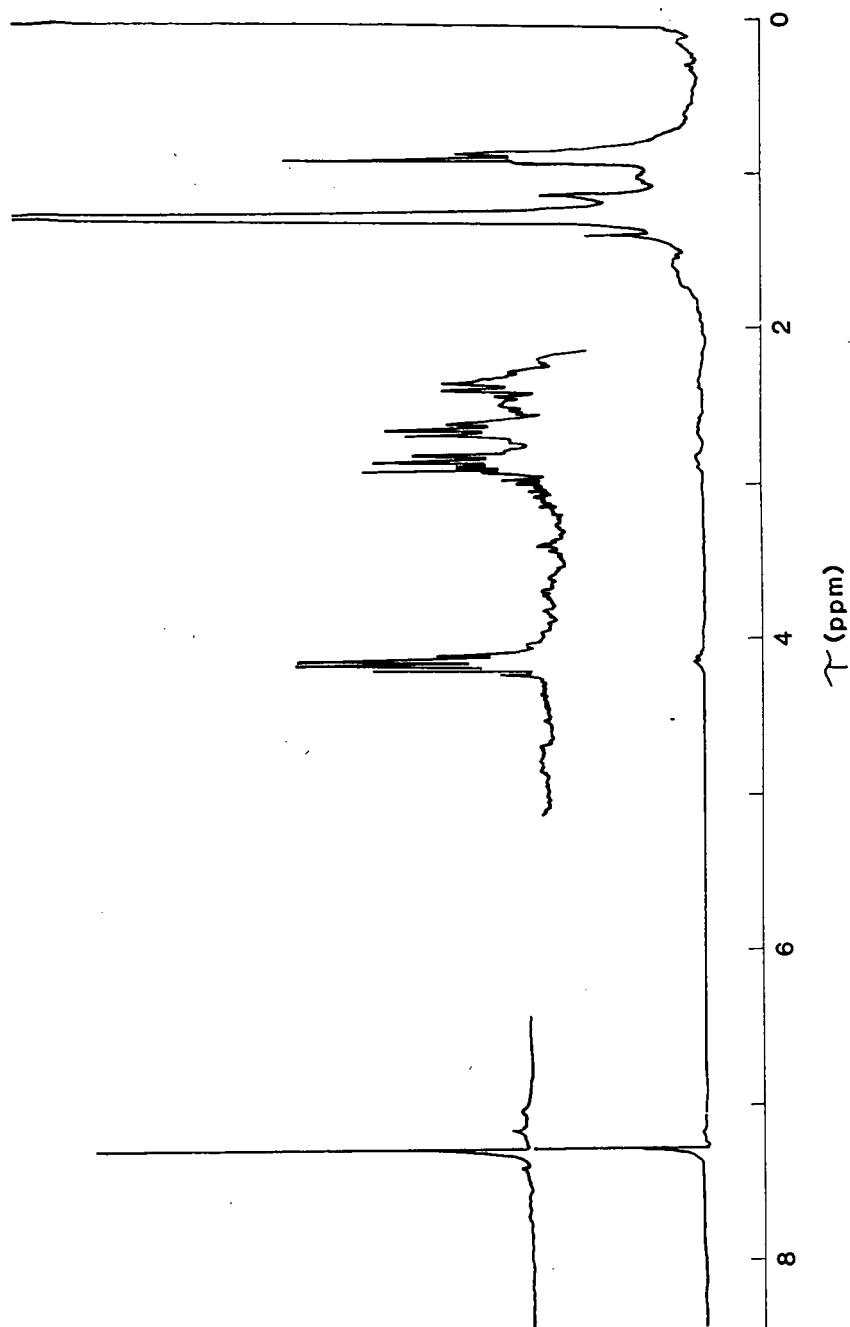
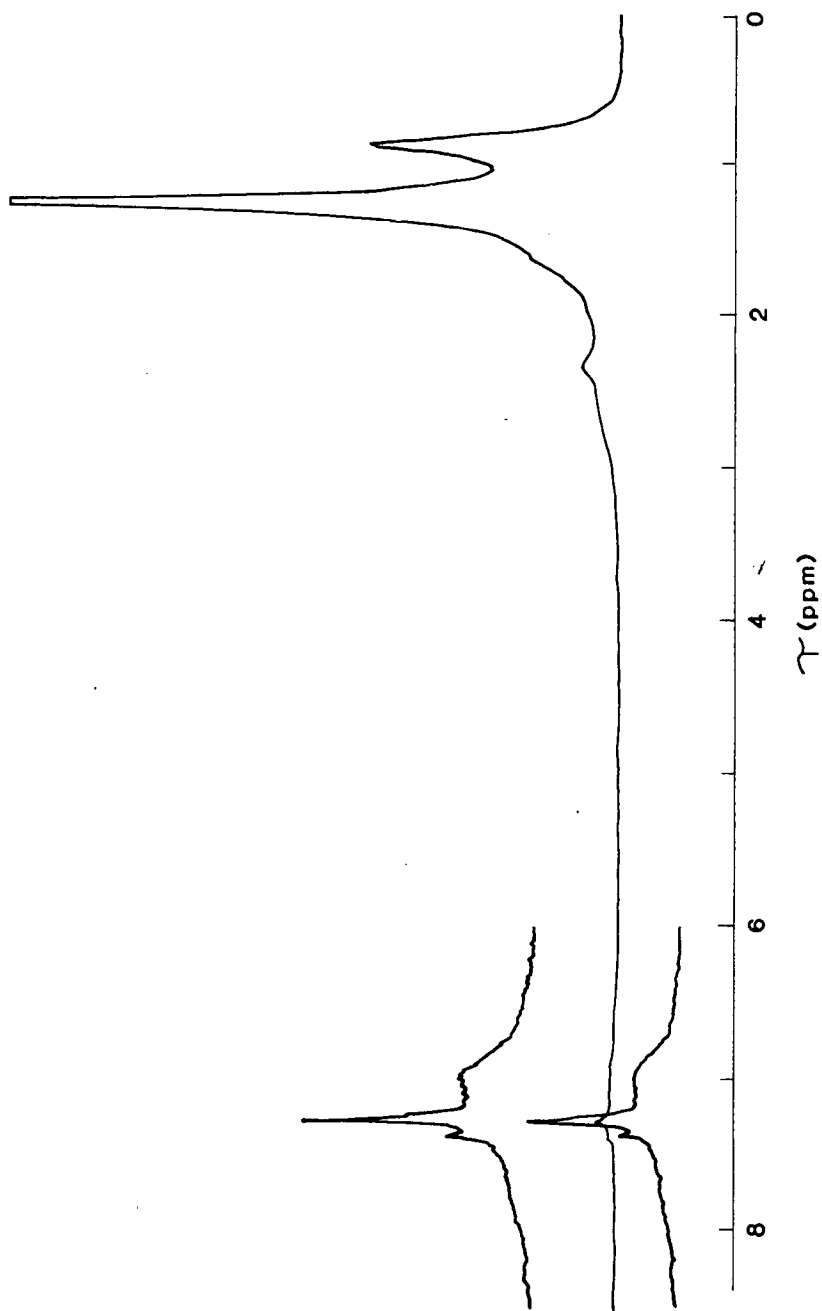


Figure 3b. ^1H -NMR Spectrum of bitumen from 44 GPT Green River
(Mahogany Zone) oil shale



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